Luminescence characteristics of $PrCl_3:Ce^{3+}$

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$PrBr_3:Ce^{3+}$ was recently introduced as a new fast scintillator [1]. Its scintillation decay curve is non-exponential. The optically excited 5d state of Ce^{3+} shows 6 ns decay time constant at room temperature (RT), which is faster than the 15 ns of $LaBr_3:Ce^{3+}$ [2,3]. The decay time constant of the Ce^{3+} 5d state of $PrBr_3:Ce^{3+}$ at 10 K is 11 ns. The 5 ns shortening of the Ce^{3+} 5d decay time when the temperature increases from 10 K to RT points to Ce^{3+} emission quenching, and the reason of the low light yield in $PrBr_3:Ce^{3+}$ [1]. To understand the nature of this quenching, we studied the scintillation and luminescence properties of $PrCl_3:Ce^{3+}$.

$PrCl_3:Ce^{3+}$ crystallizes in the same structure as $PrBr_3:Ce^{3+}$ (UCl_3 type structure with space group $P6_3/m$). The crystals are hygroscopic. Emission and excitation spectra were recorded at the SUPERLUMI station of HASYLAB. Details of this setup were described elsewhere [4].

Fig. 1a shows the emission spectra of $PrCl_3:5\%Ce^{3+}$. With a photon excitation at 4.43 eV and recorded at 10 K, $PrCl_3:5\%Ce^{3+}$ exhibits d-f doublet emission of Ce^{3+} peaking at 3.43 and 3.67 eV, see dashed lines in Fig. 1a. Compared to $LaCl_3:Ce^{3+}$, the Ce^{3+} emission is 0.1 eV shifted to lower energy. When we excite at 5.74 eV, Pr^{3+} 4f→4f transition lines are also present in the spectrum. These lines originate from the $^3P_0$ state. These lines were previously reported for undoped $PrCl_3$ and $PrBr_3$. The absence of the emission from the $^3P_1$ state has been attributed to the energy exchange with neighboring Pr^{3+} ions [5].

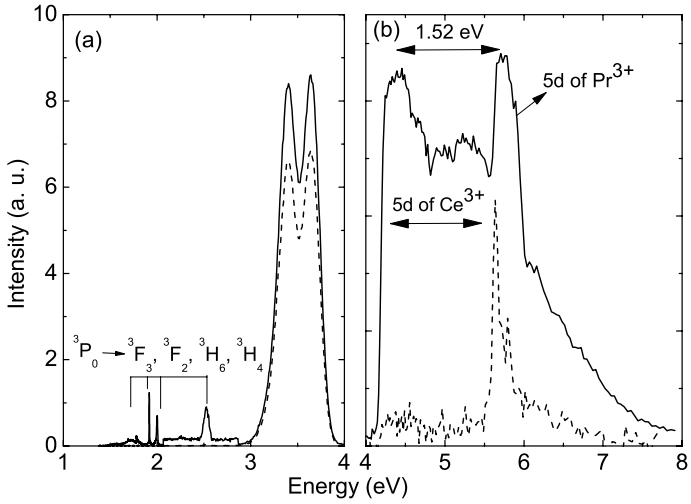

Figure 1: (a) Emission spectra of $PrCl_3:5\%Ce^{3+}$ excited at 5.74 (solid line) and at 4.43 eV (dashed line) and (b) excitation spectra of $PrCl_3:5\%Ce^{3+}$ monitoring 3.69 (solid line) and 2.53 eV (dashed line) emission. All spectra were recorded at 10 K.

The excitation spectra of $PrCl_3:5\%Ce^{3+}$ are shown in Fig. 1b. The excitation spectrum monitoring Ce^{3+} emission at 3.69 eV shows several bands between 4.13 and 5.91 eV, see solid line in Fig. 1b. The bands between 4.13 and 5.39 eV are assigned to the interconfigurational $Ce^{3+}[Xe]4f^1 \rightarrow [Xe]5d^1$ transitions. A different band at 5.74 eV also appears in the excitation spectrum monitoring the Pr^{3+} $^3P_0 \rightarrow {}^3H_4$ transition at 2.53 eV, see dashed line in Fig. 1b. This band is assigned to the $4f \rightarrow 5d_{lowest}$

transition of Pr^{3+}. The assignment is based on the estimation of the energy of the $4f \rightarrow 5d_{lowest}$ transition of Pr^{3+} from that of $4f \rightarrow 5d_{lowest}$ transition in Ce^{3+}. The Pr^{3+} $4f^1 5d^1$ bands are always about 1.52 eV higher in energy than those of Ce^{3+} [6].

Fig. 2 shows decay curves of $PrCl_3$:5% Ce^{3+} monitoring Ce^{3+} emission of 3.69 eV excited via the 5d band of Ce^{3+} at 4.43 eV recorded at 10 K and RT. The scintillation decay curve of $PrCl_3$:5% Ce^{3+} under ^{137}Cs 662 keV γ-ray excitation recorded at RT is shown in the inset. Details of the scintillation decay time setup are given elsewhere [1]. Both decay curves of Ce^{3+} emission excited via the 5d band of Ce^{3+} at 10 K and RT show a single exponential of 12 ns. Unlike $PrBr_3$:5% Ce^{3+}, $PrCl_3$:5% Ce^{3+} does not show Ce^{3+} emission quenching between 10 K and RT. The scintillation decay curve shows two components of 17 and 230 ns. Their contributions to the total light yield are 80 and 20 %, respectively. The 5 ns difference between the 12 ns decay time of the 5d excited state of Ce^{3+} and the 17 ns fast component of the scintillation decay curve implies that the main transfer from the host to Ce^{3+} takes place in about 5 ns.

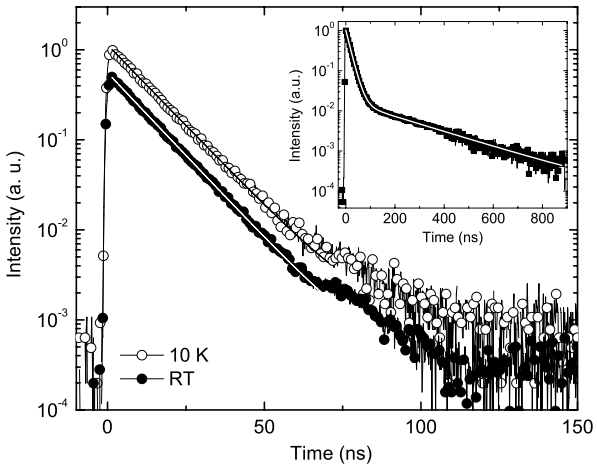

Figure 2: Decay curves of $PrCl_3$:5% Ce^{3+} monitoring emission of 3.69 eV excited at 4.43 eV. Decay curves with empty circles (o) were recorded at 10 K whereas those with solid circles (•) were recorded at RT. The inset shows the scintillation decay curve under ^{137}Cs 662 keV γ-ray excitation recorded with single photon counting method at RT. Solid lines through the data are mono- and biexponential fits.

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